Notes

Amino Acid–Cobalt(III) Complexes of N,N′–Dimethylethylenediamine–N,N′–di–α–propionic Acid

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We have previously reported the synthesis of the *uns-cis* isomer of the dichloro cobalt(III) complex of N,N′-dimethyl-ethylenediamine-N,N′-di-α-propionato(dmedpa) ligand, *uns-cis*-$(Co(dmedpa)Cl_2)^-$. The dmedpa cobalt (III) complexes of trifunctional amino acids such as L-methionine (L-met), s-methyl-L-cysteine (L-smc), L-aspartic acid (L-asp), and L-glutamic acid (L-glu) are of interest because only two of the three functional groups present in those amino acids can bind to the cobalt(III) complexes of dmedpa. In this work we wish to report the synthesis of the dmedpa cobalt(III) complexes of these trifunctional amino acids.

Experimental

Preparation of *uns-cis*-(S-methyl-L-cysteinato)(N,N′-dimethylethylenediamine-N,N′-di-α-propionato)cobalt(III), *uns-cis*-[Co(dmedpa)(L-smc)]. A solution containing 0.54g(1.5mmol) of uns-cis-$[Co(dmedpa)Cl_2]^{-1}$ in 30 m*l* of water was heated at 60 °C for 20 min. To this solution was added a solution containing 0.2g(1.5 mmol) of S-methyl-L-cystein in 10 m*l* of water. The pH of the solution was adjusted to 8.5 by addition of 1.0 N NaOH aqueous solution. After 0.1g of activated charcoal was added to the solution, the mixture as mechanically stirred at 60 °C for 4 hr. The charcoal and insoluble material were removed by filtration and washed with hot water. The combined filtrate and washings were concentrated to *ca.* 2m*l* with a rotary evaporator. The resulting violet solution was poured into a column contining cation-exchange resin (Dowex 50W-X4, 200-400 mesh, H^+ form). The complex was eluted with distilled water. The substance was concentrated to a small volume, and to this solution was added ethanol and ether. The resulting crystals were collected, washed with ethanol, and then dried. Yield. 0.29g(44%). Anal. Calcd. for $CoC_{14}H_{26}O_6N_3S$: C, 39.7: H, 6.2; N, 9.9. Found: C, 39.8; H, 6.4; N. 9.6.

Preparation of *uns-cis*-(L-Methioninato)(N,N′-dimethylenediamine-N,N′-di-α-propionato)cobalt(III), *uns-cis*-[Co(dmedpa)(L-met)]. The complex was prepared in the same way as that used for (Co(dmedpa) (L-smc)] using L-methione in place of S-methyl-L-cysteine. Yield. 0.24g(37%). Anal. Calcd for $CoC_{15}H_{28}O_6N_3S$: C, 41.2; H, 6.5; N, 9.6. Found: C, 41.3; H, 6.5; N, 9.5.

Preparation of uns-cis-(L-Hydrogen aspartato)(N,N′-dimethylethylenediamine-N,N′-di-α-propionato)cobalt(III), uns-cis-[Co(dmedpa)(L-asp)]. The complex was prepaed in the same way as that used for [Co (dmedpa) (L-smc)] using L-aspartic acid in place of S-methyl-l-cystein. Yield: 0.06g (10%). Anal. Calcd for $CoC_{14}H_{24}O_8N_3$: C, 39.9; H, 5.7; N, 9.8. Found: C, 39.8; H, 5.5; N, 9.8.

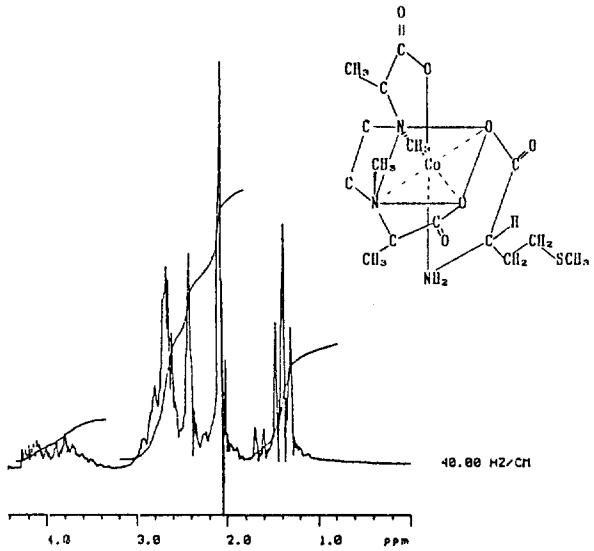

Figure 1. The ^1H-NMR spectrum of uns-cis-[Co(dmedpa) (L-met)] complex in D_2O

Preparation of *uns-cis*-(L-Hydrogen glutamato)(N,N-dimethylethylenediamine-N,N′-di-α-propionato)cobalt(III), *uns-cis*-[Co(dmedpa)(L-glu)]. The complex was prepared in the same way as that used for [Co(dmedpa)(L-smc)] using L-glutamic acid in place of S-methyl-L-cysteine. Yield. 0.42g(64%). Anal. Calcd for $CoC_{15}H_{26}O_8N_3$: C, 41.4; H, 6.0; N, 9.7. Found: C, 41.5; H, 5.9; N, 9.6.

Results and Discussion

The amino acid cobalt(III) complexes of dmedpa have been prepared from the reaction between the *uns-cis*-$(Co(dmedpa)Cl_2)^-$ complex and the amino acids used here: L-smc, L-met, L-glu, L-asp.

The fact that the [Co(dmedpa)(L-met)] prepared in this work has the *uns-cis* configuration is clearly shown in the ^1H-NMR spectra. (Figure 1) The methyl protons at the α-carbon atom are shown as two doublets at near 1.5 ppm, the proton at the α-carbon atom is shown as two quartets at near 3.8 ppm. The methyl protons at the sulfur atom are shown as a singlet at 2.1ppm. The *uns-cis* isomer has only C_1 symmetry and the two propionato arms are no longer equivalent in he *uns-cis* geometry. Therefore the methyl protons and the proton of the α-carbon atom in the planar carboxylate arm no longer lie in the same shielding area of the C-N bond and such loss of shielding would cause the methyl protons and the proton to resonate at lower fields with, respectively, two quartets and two doublets.[2-4] If the

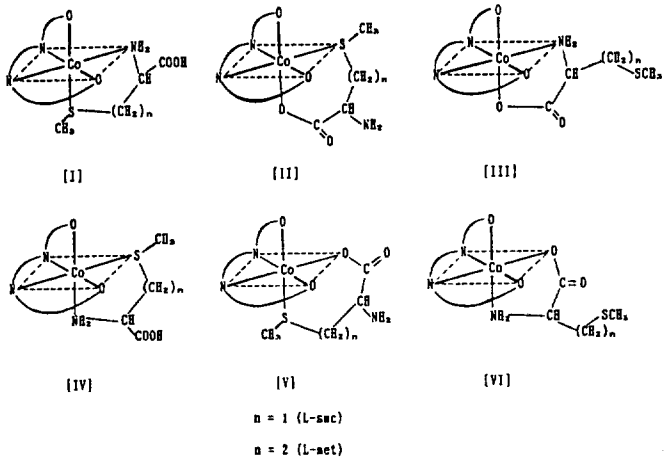

Figure 2. The geometrical isomers of [Co(dmedpa)(L-aa)] where L-aa is S-methyl-L-cysteine or L-methionine.

Table 1. The COD Stretching Frequencies of the Co(III) Complexes (cm^{-1})

Compounds	*(C=O)**	(C-O)*
dmedpa	1730	1450
uns-cis-$[Co(dmedpa)Cl_2]^{-1}$	1625	1385
Δ-uns-cis-[Co(dmedpa)(L-asp)]	1740*, 1662	1380
Δ-uns-cis-[Co(dmedpa)(L-asp)]	1715*, 1650	1395
Δ-uns-cis-[Co(dmedpa)(L-smc)]	1650	1390
Δ-uns-cis-[Co(dmedpa)(L-met)]	1650	1395

*These correspond to $\nu_a(COO^-)$ and $\nu_s(COO^-)$ of the symmetrical COO^- group. **Uncoordinated COOH stretching band.

Table 2. Electronic Absorption Spectral Data for Aquous Solutions of the Cobalt(III) Complexes

Compounds	Absorption maxima [nm(ε, $M^{-1}cm^{-1}$)]
uns-cis-$[Co(dmedpa)Cl_2]^-$	598(97), 419(68)
Δ-uns-cis-[Co(dmedpa)(L-asp)]	541(73), 380(96)
Δ-uns-cis-[Co(dmedpa)(L-glu)]	542(92), 382(123)
Δ-uns-cis-[Co(dmedpa)(L-smc)]	546(91), 379(124)
Δ-uns-cis-[Co(dmedpa)(L-met)]	542(105), 371(185)

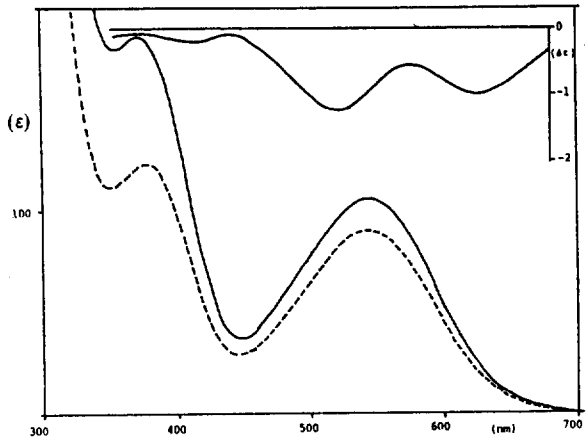

Figure 3. CD spectra and electronic absorption spectra of [Co(dmedpa)(L-met) (——) and [Co(dmedpa)(L-smc)] (-----).

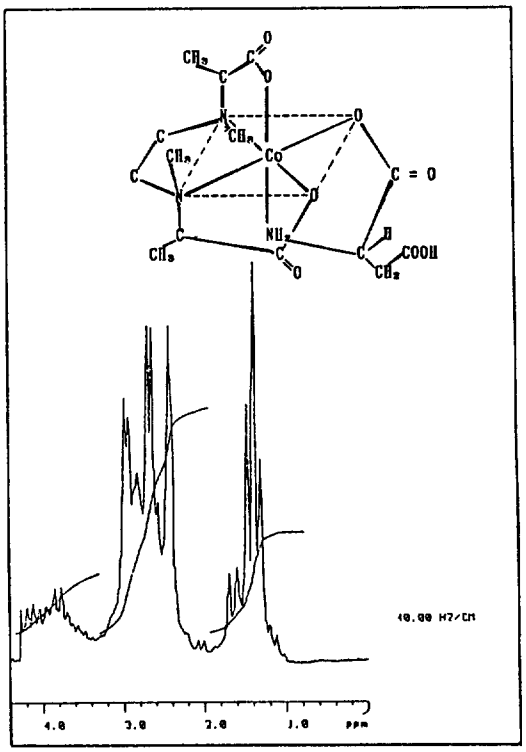

Figure 4. The ^1H-NMR spectrum of *uns-cis*-[(dmedpa) L-asp)] complex in D_2O.

complex has the *s-cis* configuration, the same methyl protons at the α-carbon atoms would have shown a single doublet and the proton should have shown a single quartet.

There are six possible modes of chelation when L-met or L-smc reacts with *uns-cis*-$[Co(dmedpa)Cl_2]^-$ as shwon in Figure 2.

Table 1 shows the COO stretching frequencies for the dmedpa ligand and the complexes prepared in this work. While the dmedpa ligand shows the free -COOH group at 1730 cm^{-1}, L-met or L-smc complex indicates that coordinated $-COO^-$ at 1650cm^{-1}, which rules out structure I, IV.[5]

From the electronic absorption spectra structure II, V also are elliminated. (Figure 3). If an S atom is coordinated, the visible spectra of $[CoN_2O_3S]$ would have shown the d-d transitions at much longer wavelengths (~600 nm) than those observed in this work, reflecting the relative positions of the groups in the spectrochemical series, $-S^- <$ amine $< -CO_2$.[6] The mer and fac isomers can be assigned from their d-d electronic absorption spectra; the holohedrized symmetry of the fac isomer is cubic, whereas that of the mer isomer is rhombic. The former can be expected to show a sharp first absorption band and the latter a broad one.[7,8] In the absorption spectra the shape of the first and is symmetry. The uns-cis-fac configuration (structure VI) is therefore, assigned to the [Co(dmedpa)(L-met)] and [(Co(dmedpa)(L-smc) complexes.

In the ^1H-NMR spectra of [Co(dmedpa)(L-asp)] the methylene protons of the aspartic acid show the doublet at 2.9 ppm and the methyl protons at the α-carbon atom show the two doublets are near 1.3 ppm. (Figure 4) Infrared spectra of [Co(dmedpa)(L-asp)] complex also has the *uns-cis*

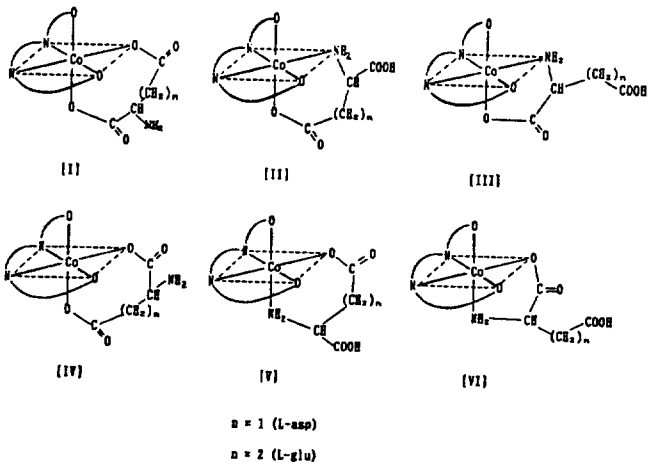

Figure 5. The geometrical isomers of [Co(dmedpa)(L-aa)] where L-aa is L-aspartic acid or L-glutamic acid.

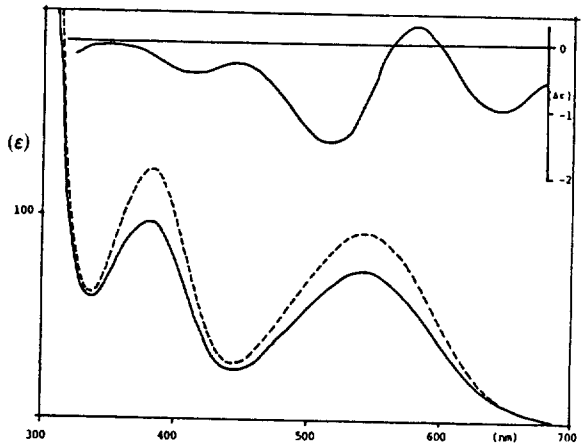

Figure 6. CD spectra and electronic absorption spectra of [Co(dmedpa)(L-asp) (——) and [Co(dmedpa)(L-glu)] (- - - -).

configuration. In the *uns-cis* dmedpa cobalt(III) complex there are six possible geometrical isomers resulting from different modes of coordination of the L-glu or L-asp (Figure 5) infrared spectra of L-asp or L-glu complex show an uncoordinate -COOH at 1740 cm^{-1} and a coordinated -COO at 1662 cm^{-1} indicating the fact that the complex excludes the structure I. IV. In the absorption spectra the shape of the first band is symmetry. The *uns-cis-fac* configuration (structure VI) is, therefore, assigned to the [Co(dmedpa)(L-asp] (Co(dmedpa)(L-glu) complex (Figure 6).

The CD spectra of the complexes prepared in this work show the negative dominant peak in the T_{1g} region, indicating the fact aht all of the [Co(dmedpa)(L-aa)] complexes have the Δ configuration.[9,10]

It is noted that the substition reactions of the *uns-cis*-$[Co(dmedpa)Cl_2]^-$ with amino acids gave products with retention of configuration. The kinetic inertness of the dmedpa-Co(III) chelate inhibiits the isomerization of the complex when the dichloro is displaced and leads to retention of configuration in going from the dichloro to amino acid complexes.

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